PRESOLAR GRAPHITE IN THE NANOSIMS: A DETAILED LOOK AT THE ISOTOPIC MAKEUP OF THE SPHERULE AND ITS SUB-COMPONENTS. F. J. Stadermann, T. Bernatowicz, T. K. Croat, E. Zinner, S. Messenger and S. Amari, Laboratory for Space Sciences and Physics Department, Washington University, St. Louis, MO 63130-4899, USA.

Introduction: The new NanoSIMS ion microprobe allows isotopic measurements of sub-micrometer sized features in TEM thin sections. This makes it possible for the first time to take an 'inside look' at isotopes in presolar graphite spherules from supernovae [1-3]. We find that the NanoSIMS does reproduce previous bulk isotopic measurements, makes measurements of internal isotopic gradients possible, and is capable of determining the isotopic composition of 200 nm sized sub-components, such as internal TiC crystals.

Samples: The TEM slices used in this study are from a large (12 µm) presolar graphite spherule (KE3e#10) from the Murchison (CM2) density separate KE3. Bulk isotopic measurements with the ims3f ion microprobe have identified this grain as having a supernova origin [1]. A study of 37 TEM sections from this spherule revealed abundant internal TiC crystals with mean diameters ranging from 30 to 500 nm [1]. Five of these sections containing 4 TiC crystals were selected for detailed NanoSIMS analysis.

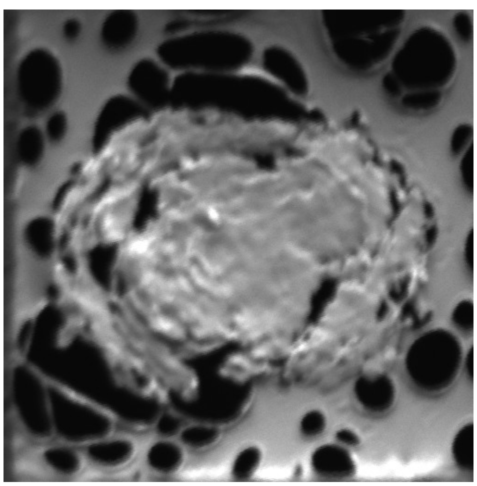

Figure 1. Secondary electron image of one of the graphite slices, acquired during the NanoSIMS isotopic measurements. The field of view of all images is 12 x 12 µm^2.

Experimental: For the measurements in the NanoSIMS, entire carbon-coated TEM grids were attached to flat sample holders. This leaves the samples supported only by the thin (20–30 nm) carbon films on the TEM grids. Since SIMS is a destructive measurement technique, the carbon film will eventually tear, setting an analysis time limit for the measurements. We found that under typical NanoSIMS measurement conditions with a 0.5 pA primary beam rastered over 15 x 15 µm^2, a TEM section can last up to 10 hours. This, together with the high sensitivity and the multidetection-capabilities of the NanoSIMS makes it possible to determine the isotopic composition of several elements in imaging mode at a lateral resolution of around 100 nm. Simultaneously with the secondary ions, secondary electrons are also detected (Fig.1), which give a detailed picture of the surface morphology. Figure 1 also shows the carbon film surrounding the graphite grain. The holes grow during the analysis, indicating that the support film is beginning to tear long before the actual sample material is exhausted.

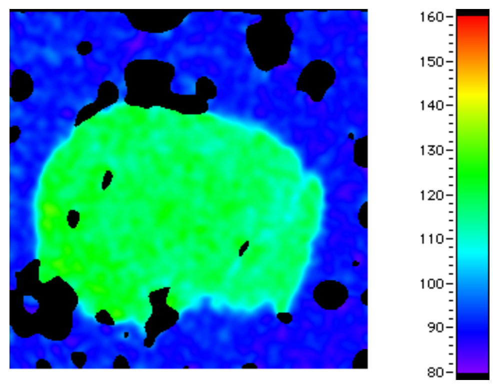

Figure 2. False color image of the carbon isotopic ratio. The surrounding C film is used as isotopic standard, whose composition is terrestrial, i.e. $^{12}C/^{13}C$=89. This particular slice does not have any embedded TiC crystals.

Results: The internal C isotopic composition of a near-surface section from the graphite spherule is shown in Figure 2. The grain appears fairly homogeneous in this image and the overall composition of $^{12}C/^{13}C$ = 118 agrees with the previous ims3f bulk measurements of $^{12}C/^{13}C$ = 125 (the small difference can be attributed to the different standards used to correct for instrumental mass fractionation).

A detailed look at the C and O isotopic ratios within this grain showed that there appears to be a uniform gradient from the center to the outside. This gradient becomes more visible, when the grain is subdivided into five concentric regions with region 1 representing the center and the others forming rings around it. Region 5 is the outermost part of the grain in this TEM section. The averaged isotopic compositions of the different regions are shown in Figure 3. There is a pronounced gradient in the $^{16}O/^{18}O$ ratio, with outer regions becoming increasingly more 'terrestrial'. A corresponding, but much smaller trend can be seen in the $^{12}C/^{13}C$ ratio, while the $^{16}O/^{17}O$ ratio shows no variation but has much larger errors. While it is tempting to attribute these internal gradients to the particle's growth history, indicating an isotopically changing environment during its formation, the gradients are more likely an indication of different degrees of exchange with the surrounding (isotopically normal) material. Nonetheless, this measurement nicely illustrates the suitability of the NanoSIMS for such analyses. That the $^{16}O/^{18}O$ ratio does not quite reach the value of 174 measured in the ims3f in the center region is most likely due to the fact that this particular TEM slice is from near the surface of the graphite spherule and does not go through its center.

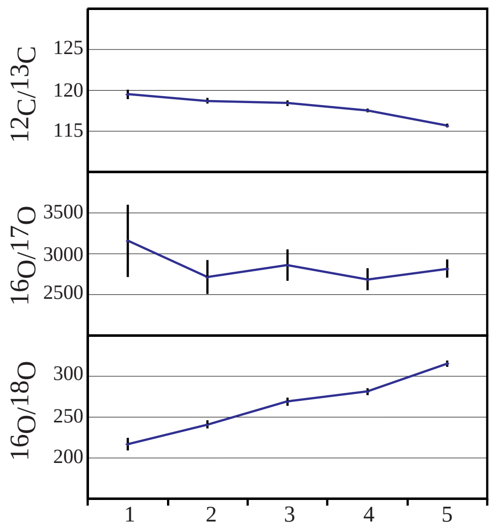

Figure 3. Distribution of the oxygen and carbon isotopic compositions in the different regions discussed in the text. The errors shown are strictly Poisson errors based on the integrated counts in individual regions. The terrestrial values are 89, 2696, and 489, respectively, for the three ratios shown.

The small sizes of the internal TiC crystals present in some of the TEM sections of this graphite pose a special challenge. Surprisingly, however, these grains are very easy to find in the secondary oxygen images (see Fig. 4 + 5). At this point it is not clear why a high oxygen signal is associated with these TiC crystals. The oxygen isotopic compositions of these two grains are enriched in ^{18}O and clearly presolar, indicating that the high oxygen signal is not due to chemical reaction with terrestrial material during laboratory procedures. The carbon isotopic compositions of the TiC grains are indistinguishable from those of the surrounding graphite. We have not yet measured the Ti isotopes in these tiny grains, but plan to do so in the future.

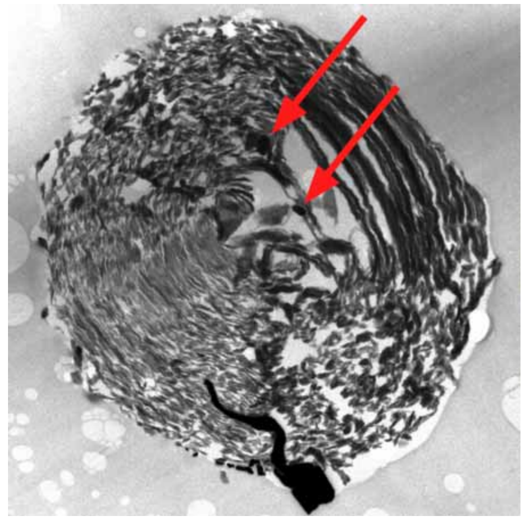

Figure 4. TEM image of a central section from the same graphite spherule, with two internal TiC grains (arrows).

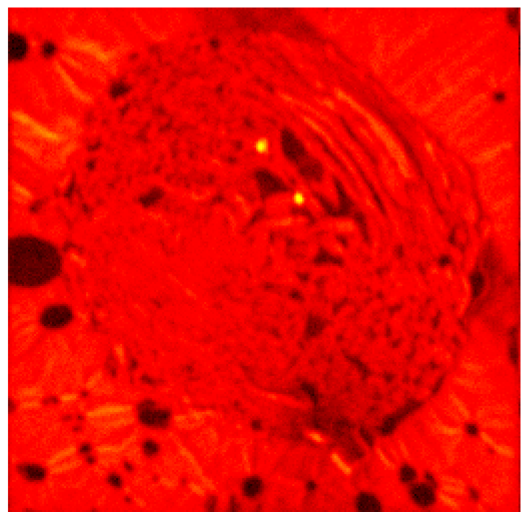

Figure 5. This image shows the ^{16}O secondary ion signal of the same area as Figure 4 during a NanoSIMS measurement of this slice. The two TiC grains are clearly visible as the bright spots with a high oxygen signal.

Conclusions: The NanoSIMS is very well suited for the kind of detailed isotopic studies reported here. We have shown that an internal isotopic gradient in this graphite grain can be detected. In addition, it is possible to measure the isotopic makeup of 200 nm TiC crystals, which constitute an abundant subcomponent in some of these graphites.

References: [1] Croat T. K. et al (2002) *Lunar Planet Sci.* **XXXIII** *(this volume)*. [2] Bernatowicz T. et al. (1998) *Lunar Planet Sci.* **XXIX**, Abstract #1393. [3] Bernatowicz T. et al. (1999) *Lunar Planet Sci.* **XXX**, Abstract #1392.